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POTENTIALLY TOXIC ELEMENTS AND RARE EARTH ELEMENTS IN PLANTS FROM THE LAKE KALIMANCI BANK (NE REPUBLIC OF MACEDONIA)

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A b s t r a c t: Potentially toxic elements (PTE) and rare earth elements (REE) are often increased in the environment, especially nearby active or abandoned mines. While NE Macedonia is very rich with metal ore bodies also elevated pollution is expected in the surrounding ecosystems. NE part of the country is also very important agricultural area where several food crops are being produced and consequently water from local lakes and rivers is being used for irrigation. In present paper we have focused on different plant species growing on the Lake Kalimanci bank. All plant species were analyzed for PTE and REE. Results revealed that the PTEs (Cr, Cu, Pb, Zn, Ni, As and Cd) in the studied plant species show great enhancement in all samples and also exceed the recommended and allowable limits. Meanwhile REEs reflect a very similar range among all samples. Generally, all REEs were in the safe range, according to currently known regulations.

Key words: Lake Kalimanci; geochemistry; plant species; transfer factor

1. INTRODUCTION

1.1. *PTE in flora*

Man has used many metals for centuries, but only in the last few decades have the possible effects of metals on the environment and on human health been studied by Yi et al. [1], Mitra et al.[2], Mendil et al. [3], Alkan et al. [4], Jabeen & Chaudhry [5]. PTE are introduced into the environment (e.g. aquatic systems) as a result of weathering of rocks and soils (Adeyeye et al. [6]), so the highest contents of PTE are in metal-rich areas, such as ore-rich deposits. Other than natural sources, the major causes of PTE concentrations in the environment are mining activity and other anthropogenic contributions (industry, traffic, etc.). Mine waters (all natural waters emanating from a mine site, including tailing dams and their leachates) are a part of the water cycle (Riba et al., [7]), and when they are without adequate treatment, aquatic environments can be seriously affected. Once PTE enter an aquatic ecosystem, the uptake of PTE can occur in all living organisms. Even though some PTE are essential for living organisms (e.g. copper (Cu), zinc (Zn), iron (Fe)), they can also be toxic; if the concentrations are too low or too high, they may equal the toxicity of non-essential metals (e.g. tin (Sn), aluminium (Al), cadmium (Cd), mercury (Hg), lead (Pb)) (Kennedy [8]). Aquatic organisms have a dynamic relationship with the environment and the bioavailability of PTE is also influenced by chemical speciation in the surrounding matrix. It is suggested that both organisms and their surrounding environment (water, sediments) should be studied together to investigate possible metal toxicity.

Beside many essential macronutrients (P, K, N, Ca, S) and micronutrients (Fe, I, Mn, Ni, Zn, Cu, Co, B, Mo) in the soils and sediments, PTEs can be

found and are therefore available for plants. Sometimes concentrations of PTE exceed the maximum allowable levels of those elements found in soils and sediments. Therefore there exists a threat to plants, which have the ability to accumulate PTEs when they are grown in polluted areas or are irrigated with polluted water. Hundreds of plant species of different families have been determined to have a high genetic capacity to accumulate and tolerate large amounts of PTE, and these are known as hyperaccumulator species. These plants are mainly used for phytoremediation processes of contaminated lands, but are also great indicators of possible pollution. PTE accumulation in plants may pose a direct threat to human health (Türkdogan et al., [9]). According to Zurera-Cosano et al. [10], plants can take up PTE by adsorbing them from contaminated lands, as well as from deposits on different parts of the plants exposed to the air from polluted environments. Islam et al. [11] reported that nearly half of the mean ingestion of Pb, Cd and Hg through food is of plant origin (fruits, vegetables, cereals). Although the present study does not deal with edible plants, it is important to evaluate the approximate uptake of PTE into the different plant species in order to assess the potential health risk for the inhabitants. For instance, plants like *Mentha arvensis* are often used by locals for tea.

1.2. *REEs in flora and their health effects*

The world's scientific literature lacks studies concerning the general effects of REE in flora, as well as studies of the health effects of REE. Anan et al. [12] report that REEs have recently been widely used in agriculture as fertilizers to improve crop growth and production, and consequently the increase of REEs in agricultural soils was determined. Meanwhile, there is not enough knowledge about treating REEs after their use for different purposes, and their widespread use has led to their accumulation in the environment. Some researchers (Wang et al. [13], etc.) have worked with different plants to establish hyperaccumulator plants for REE.

Nevertheless, there are still no special indicators established yet which could provide us with information about REE, and whether they are essential or non-essential to living organisms (plants, animals, humans). In 2004, Fan et al. [14] explained that children who were exposed to REE had lower immunoglobulin M (IgM) and that children's IQ increased with the distance from the exposure. In addition, they discovered that children from an REE ore area have a higher burden in the body and exposure to REE could have adverse influences on the children. In April 2012, the US Environmental Protection Agency (US EPA) [15] published an REE review with the key findings that: (1) the waste footprint and environmental impacts from mining to extract REE mineral ores are expected to be as significant as current metals/minerals mining practices. The most significant impact from contaminant sources associated with hard rock mining is to surface water and ground water; (2) REE milling and processing is a complex, ore-specific operation that has potential for environmental contamination when not controlled and managed properly – from heavy metals and radionuclides in waste streams; (3) the specific health effects of elevated concentrations of REEs in the environment from mining and processing REE-containing materials are not well understood – most data reviewed were for mixtures and not individual elements. In recent years the US EPA has established assessment regulations for cerium (2009), gadolinium (2007), lutetium (2007), neodymium (2009), praeseodymium (2009), promethium (2007) and samarium (2009), but there is still a need to define basic regulations for lanthanum, europium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, scandium and yttrium. There is still also limited information about the carcinogenic potential of REEs. Therefore, a lot of research works need to be done to establish additional support for human health toxicity and ecological studies on specific REEs as well as to use this information to conduct site risk assessments related to REE mining, processing and recycling. Therefore every study dealing with REE is one step closer to a better understanding of their behaviour and side effects.

The area around Lake Kalimanci has been under high mining influences for decades. In its close vicinity several metal mines are located (e.g. Sasa-Toranica and Kratovo-Zletovo ore district; Figure 1). Not only geological composition of bed rocks and metal mineralization, but also heavy traffic and environmental disasters influence lake ecosystem. In the past water, sediment and fishes from Lake Kalimanci were analyzed and presented by Vrhovnik et al. [16–19]. To compelte evaluation of metal contents (PTE, REE) also plants from Lake Kalimanci embankment were taken into consideration.

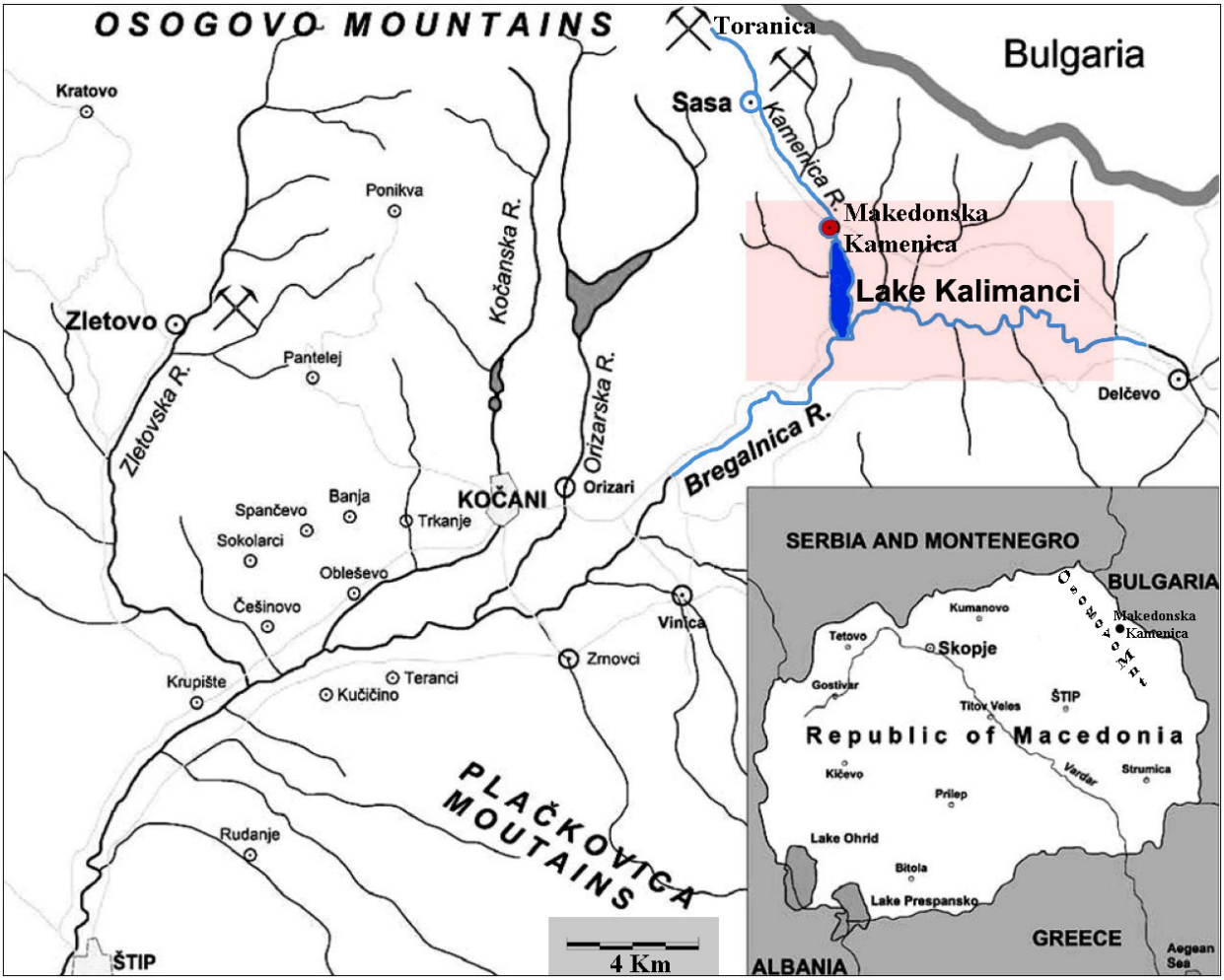

Fig. 1. Study area

2. MATERIALS AND METHODS

2.1. *Study area*

Serbo-Macedonian Massif extends from Republic of Serbia, through eastern part of Republic of Macedonia to the Lake Dojran on the southern border with Greece (Figure 2). Serbo-Macedonian Massif is located between Hellenides, Vardar Zone and Rhodope Massif (Meinhold et al. [20]) and is mainly combined by Precambrian, Riphean-Cambrian and Paleozoik metamorphic rocks (Serafimovski et al. [21]) (Figure 2). The beginning of the tectono-magmatic activation took place in the middle Oligocene and repeated in Plio-Pleistocene. The largest polymetal metallogenic zone in Osogovo Mountains is Sasa-Toranica deposit, but there are more small-sized metallogenic developments on south-eastern part. Sasa deposit lies close to Bulgarian border, and is hosted by metamorphic and volcanic rocks (different gneisses, quartz graphite, chlorite-sericite schists with interbedded limestones (Serafimovski et al. [22]). Ore bodies are located at the contact between quartz-graphite schists and gneisses, limestones or quartz latites. The length of ore bodies in Sasa ore district varies from 150 to 1800 m, and their thickness varies from 1 to 20 m (Serafimovski et al. [22]). In Sasa ore deposit skarns were formed under 600–400ºC, and they occurred with vollastonite, bustamite, garnet and rodonite (Serafimovski et al. [22]). According to Serafimovski et al. [22] and Vrhovnik et al. [23] are in the Sasa ore district most common metalliferous minerals pyrite, sphalerite and galena with some accessories minerals like pyrrothite, chalcopyrite, magnetite and marcasite. Rarely there also occur hematite, Ag- and Bi-bearing minerals. Sasa mine has been in production for over 45 years yielding 90 000 tons of Pb-Zn high quality concentrate annually.

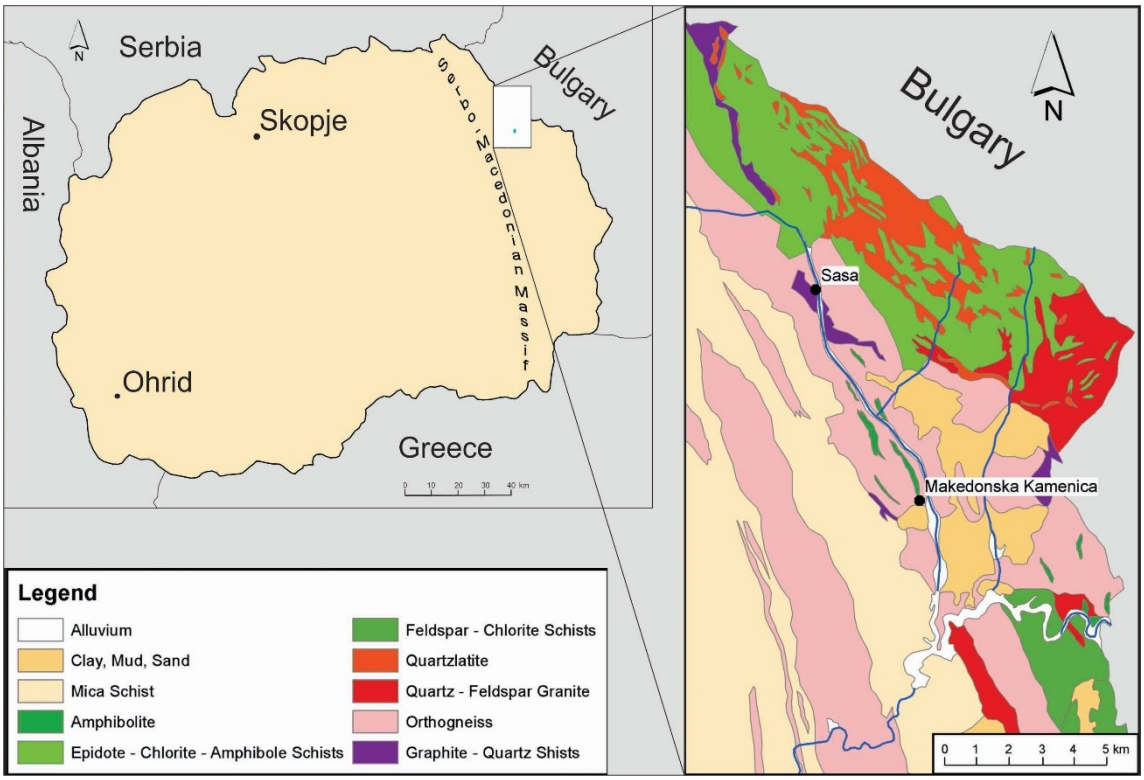

Fig. 2. Geological map of study area

The tailings material from Sasa mine is located between Sasa mine and Kamenica river, part of which flow beneath the tailings dam. Sasa tailings dam mainly consists of quartz, pyrite, galena, sphalerite, gypsum, hornblende, actinolite, albite, anortite, biotite and orthoclase (Vrhovnik et al. [23]). The tailings dam is divided in four parts, among which No. 4 is currently used and its capacity is projected of 2,000,000 m^3 of which half is filled. In year 2003 a major environmental disaster happened, when a part of Sasa tailings dam (No. 4) collapsed and caused an intensive flow of tailings material through the Kamenica river valley. Between 70 000 and 100 000 m^3 of tailings material was discharged into the Lake Kalimanci.

Artificial Lake Kalimanci extends in length 11.14 km and width 0.385 km, the maximum depth is 80 meters (Figure 3). The surface area of the lake is 4.29 km^2 and it accumulates approximately 130 million m^3 of water. According to our previous research (Vrhovnik et al. [24]), the surficial sediments from Lake Klimanci reflect the mineral composition of bedrocks from Osogovo Mountains and contain quartz, plagioclases, K-feldspars, clay minerals and occasionally hornblende, dolomite, smithsonite, galena and sphalerite, as well as authogenic minerals like goethite, hematite and pyrite. The basic purpose for building the dam in one part of the Lake Kalimanci was the need for producing energy and for irrigation of Kočani Valley, where rice and maize fields extend. Next to water from Lake Kalimanci is also used waters from the Zletovska and Bregalnica rivers, which flow through Kočani Valley.

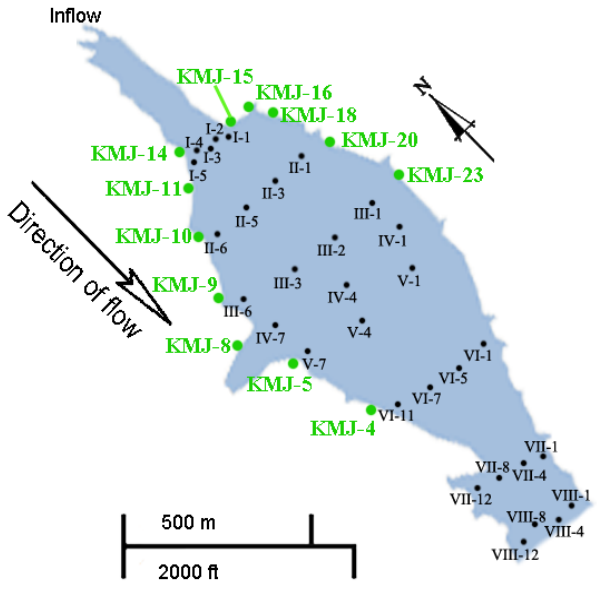

Fig. 3. Sampling locations of plant species (KMJ) with added locations of sediment samples

2.2. *Sample selection and chemical analyses*

Collection of the representative plant samples from the lake bank was established in November 2010. Plant samples were collected from the shore of Lake Kalimanci; at each location three individual plants of each species were taken. During sampling, 23 different species were collected, but for further analysis only 13 species were used, and the rest were removed for different reasons (not enough samples, damage, indefinable species, etc.). Plants were placed individually in pre-cleaned plastic bags and immediately transferred to the laboratory, where they were separated into roots and shoots. The plant material was carefully washed with tap water, followed by distillate water. After washing, plants were dipped into the 0.01 M HCl for one minute and afterwards washed with Milli-Q (ultrapure) water, to remove possible surface contamination with PTE. Afterwards plants were air dried for 10 days, and were then dried in the oven at 60°C for an additional 48 hours. The oven-dried materials were then ground to a fine powder for further analysis. Plant species were identified at the University of Maribor's Faculty of Agriculture and Life Sciences, Department of Grassland Management and Forage Production, and are presented in Table 1.

T a b l e 1

Plant species used as metal toxicity evaluating tool

Sample	Plant Species
KMJ-4	*Plantago major*
KMJ-5	*Geranium dissectum*
KMJ-8	*Euphorbia cyparissias*
KMJ-9	*Dorycnium herbaceum*
KMJ-10	*Fabaceae sp.*
KMJ-11	*Fabaceae sp.*
KMJ-14	*Mentha arvensis*
KMJ-15	*Carex sp.*
KMJ-16	*Carex sp.*
KMJ-18	*Plantago lanceolata*
KMJ-20	*Juncus sp.*
KMJ-23	*Taraxacum officinale*
*KMJ-20K	Roots of *Juncus sp.*

All plant samples were analyzed for 57 elements (major, minor, trace and REEs) at an accredited commercial laboratory, Act Labs (Activation Laboratories Ltd., Ancaster, Ontario, Canada, in year 2011), using inductively coupled plasma mass spectrometry (ICP/MS) and microwave digestion. Dry, unwashed samples were digested in Aqua Regia solution 3/1 (v/v) (HNO_3 + 3HCl) at 95°C for two hours. Resultant sample solutions were then diluted and analyzed on a Finnegan Mat Element 2 High Resolution ICP/MS (HR-ICP/MS). The quality of the analyses was monitored by comparison to the standard materials NIST 1575a, NIST 1643e and SLRS-5 provided by Act Labs and the measurements of four samples were repeated. Besides Act Lab quality control, also our own standard MP-STD-011, and two standards prepared and provided by the International Atomic Energy Agency, Vienna (IAEA) – IAEA-407, and by National Research Council Canada – DORM-3 were sent to Act Labs for geochemical analysis as well. The results indicated a good agreement between the certified and observed values. The standard deviations of the means observed for the abovementioned certified materials were 1–6 %.

2.3. *Transfer factor calculation*

To evaluate the accumulation of PTE in plants from lake ecosystem was calculated the transfer factor (TF) (Kalfakakour and Akrida-Demertzi [25], Rashed [26]). Which provide information of PTE content in plant tissue and was incorporated in plants from water and lake sediment. TF was given as:

$$TF = \frac{\text{Concentration of metal in plant tissue}}{\text{Mean concentration of metal in lake ecosystem (water or sediment/soil)}}$$

According to Kalfakakour and Akrida-Demertzi [25], a TF greater than 1 indicates bioaccumulation of metals in plant tissue.

All statistical analyses were performed using the Statistica 8 software.

3. RESULTS AND DISCUSSION

3.1.. *PTE in different plant species*

Plants growing on a metal-contaminated medium can accumulate high concentrations of PTE and so cause a serious health risk for consumers. Plant species and varieties vary in their capacity for PTE accumulation. Results of the PTE contents of twelve plant species are presented in Table 2, together with the sufficient and excessive levels adopted by Kabata-Pendias [27].

T a b l e 2

PTE in different plant species from the Lake Kalimanci embankment (mg/kg)

	Cr	Co	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag	Hg	Se
DL	10	0.1	1	10	10	100	10	1	0.1	0.1	1	1	1	100
Mean	233	3.67	3.98	26.4	144	488	73.8	9.61	5.15	0.29	0.21	0.25	0.12	0.26
Minimum	84.1	1.12	1.58	8.95	10.8	114	23.3	1.61	0.3	0.07	0.02	0.03	0.06	0.2
Maximum	1140	13.9	17.4	61.6	549	1090	404	39	14	0.95	0.67	0.79	0.27	0.4
Standard deviation	296	3.62	4.32	18.4	168	330	106	11.9	5.07	0.26	0.22	0.27	0.07	0.08
KMJ-4	84.1	1.76	1.58	23.6	175	831	23.3	4.93	8.17	0.19	0.3	0.14	0.19	0.3
KMJ-5	84.6	1.38	2.11	8.95	10.8	114	24	2.31	0.3	0.15	0.02	0.04	0.13	0.2
KMJ-8	160	5.25	2.32	9.46	11	125	53.8	4.41	0.34	0.2	0.03	0.03	0.1	0.2
KMJ-9	109	1.33	3.2	14.3	30.9	236	29	1.97	0.59	0.08	0.07	0.04	0.08	0.2
KMJ-10	93.7	1.12	2.35	10.6	17	270	31.3	1.61	0.96	0.07	0.02	0.03	0.07	0.2
KMJ-11	93.5	1.34	2.89	13.2	41.2	216	31	3.57	0.96	0.11	0.05	0.15	0.07	0.2
KMJ-14	148	2.14	2.34	31.9	177	772	39.5	6.12	7.5	0.22	0.29	0.22	0.1	0.4
KMJ-15	295	5.02	4.39	39	288	651	84.6	8.36	12.6	0.35	0.42	0.48	0.13	0.2
KMJ-16	117	1.63	2.26	29.1	83.1	616	41.5	2.78	5.75	0.11	0.13	0.42	0.06	0.3
KMJ-18	311	5.18	4.5	61.6	549	1090	80.6	29.2	9.25	0.95	0.67	0.79	0.27	0.3
KMJ-20	1140	13.9	17.4	58.4	317	728	404	11	14	0.53	0.5	0.64	0.22	0.4
KMJ-23	163	3.98	2.43	16.2	24.1	205	43	39	1.33	0.54	0.06	0.05	0.06	0.2
*KMJ-20K	1190	15	6.23	114	4.17	1300	333	29.9	20.9	1.2	1.49	2.19	0.39	0.8
** Sufficient or Normal	0.10–0.50	0.02–1.00	0.20–5.00	5.00–30.0	5.00–10.0	27.0–150	0.10–5.00	1.00–1.70	0.05–0.20	7.00 – 50.0	/	0.5	/	0.01 – 2.00
** Excessive or Toxic	5.00–30.0	15.0–50.0	10.0–50.0	20.0–100	30.0–300	100–400	10.0–100	5.00–20.0	5.00–30.0	150	/	5.00 – 10.0	1.00 – 3.00	5.00 – 30.0

PTE levels in the different plant species ranged as follows:
Cr 84.1 – 1140 mg kg^{-1}, Co 1.12 – 13.9 mg kg^{-1}, Mo 1.58 – 17.4 mg kg^{-1}, Cu 8.95 – 61.6 mg kg^{-1}, Pb 10.8 – 549 mg kg^{-1}, Zn 114 – 1090 mg kg^{-1}, Ni 23.3 – 404 mg kg^{-1}, As 1.61 – 39.0 mg kg^{-1}, Cd 0.30 – 14.0 mg kg^{-1}, Sb 0.07 – 0.95 mg kg^{-1}, Bi 0.02 – 0.67 mg kg^{-1}, Ag 0.03 – 0.79 mg kg^{-1}, Hg 0.06 – 0.27 mg kg^{-1} and Se 0.02 – 0.40 mg kg^{-1}.

Half of the studied PTE exceeded the sufficient levels adopted by Kabata-Pendias [27] and can be classified as toxic according to the aforementioned criteria. Cr, Cu, Pb, Zn, Ni, As and Cd are found to be toxic, meaning that raised contents of the listed PTE could seriously affect plants and also consequently cause harm to inhabitants from the adjacent area. All the highest PTE concentrations were measured in plant samples *Plantago lanceolata* (KMJ-18) and *Juncus* sp. (KMJ-20), which were taken from the eastern part of Lake Kalimanci between the first (I-1) and the second (II-1) profiles (Figure 3). This coincides with the highest levels of PTE in the surficial lake sediments, while PTEs in the lake water were almost equal through the lake. Furthermore, when the excess levels of Cr, Cu, Pb, Zn, Ni, As and Cd are compared with the sequential extraction results obtained from the lake surficial sediments, a clear coincidence is noted. Among the above-listed PTE, excluding the Cr for which a sequential extraction scheme was not applied, it is seen that majority, except for As, tend to be heavily available in the exchangeable fraction (leaching stage 2), meaning that they are highly bioavailable for plants under normal conditions.

According to Islam et al. [11], roots contain up to 3 times higher concentrations of PTEs than stems. The PTE content in roots of *Juncus* sp. (KMJ-20K) was also obtained (Table 2), and shows that almost all the PTEs are raised in these roots, except for Mo, Pb and Ni, of which there tends to be more in the plant stems. So far, the mechanisms of metal uptake by *Juncus* sp. are poorly understood, and depend on the metal and plant species, as well as various other factors. For these reasons, further detailed plant studies are needed to explain this still insoluble puzzle.

3.1.1. *Health risks*

The aquatic environment is a resource that must be protected and maintained in a healthy state. When the health of plants and animals that are part of the food chain is affected, there is a risk to human health (Mulligan et al. [28]). The mining industry, leaking tailing dams, atmospheric inputs, etc., are the main contributors of increasing PTE in the living environment. Waters from rivers flowing near mining activity are major transporters of contaminants to lakes and oceans. After PTEs enter an ecosystem, ingestion of bioavailable PTEs in different organisms is possible, and can lead to diseases and, at lethal doses, even to death. Bioaccumulation of PTE in the food chain poses major threats to human health, especially to children during their development. PTEs can enter the human body through inhalation, ingestion or skin contact. Therefore detailed study and evaluation of possible contaminants at the study area is needed to prevent the PTEs influencing human, animal and plant existence.

3.2. *Transfer factor (TF) and risk assessment*

Sediment/water to plant transfer is one of the key components of human exposure to PTE through the food chain. Therefore, the TF was calculated to provide information about metal content in different plant species. When the calculated TFs are above 1, this indicates bioaccumulation of PTE or REE in flora from the sediment or water (Kalfakakour & Akrida-Demertzi [25]).

TF was calculated using the equation presented by Kalfakakour and Akrida-Demertzi [25]. In cases where the concentrations were below the detection limit (DL), TF were not calculated and are marked with empty spaces. Among the REEs, Gd, Tm and Yb at a few locations have concentrations lower than the DL; only those above the DL were used for TF calculation. Data of geochemical composition of lake sediments and water were adopted from our previous works (Vrhovnik et al. [16–19]).

A plant's ability to take up PTE or REE (Table 3) from growth media (sediment) or water can be evaluated by a ratio of the element content in the plant to the element content in related media (e.g. sediment, water), so Kabata-Pendias [27] suggested the TF as the best evaluating tool. According to Cui et al. [29] individual metals can vary greatly within the plant species, as some PTE or REE are more susceptible to phytoavailability than others (Kabata-Pendias [27]). Furthermore, Kabata-Pendias [27] identified a great number of reasons for the difference in metal availability among various plant species: 1) low concentrations in solutions, 2) occurrence of H^+ and other tions, 3) stage of plant development, 4) T, pH and Eh of sediment and water, 5) selectiveness for a particular ion, etc.

T a b l e 3

The REE in different plant species

Element	Different plant species		
	Mean	Min	Max
La	4.09	1.38	11.20
Ce	8.43	2.66	23.50
Pr	0.95	0.29	2.56
Nd	2.97	0.90	7.73
Sm	0.60	0.18	1.52
Eu	0.18	0.05	0.42
Gd	0.38	0.12	0.93
Tb	0.11	0.03	0.26
Dy	0.33	0.11	0.88
Ho	0.06	0.02	0.17
Er	0.22	0.08	0.57
Tm	0.02	0.01	0.06
Yb	0.17	0.06	0.46
Lu	0.02	0.01	0.06

Table 4 summarizes the results of the calculated TF [plant/sediment] values. Mean TF PTE [plant/sediment] values are generally low and range from 0.03 (Bi) to 4.62 (Cr). Among the entire mean PTE TF [plant/sediment] values, only Cr, Mo, Ni and Hg were greater than 1, indicating that the majority of PTEs in the lake surficial sediments are poorly available to plants. This statement does not exactly correspond with the sequential extraction results, as none of the metals strongly bound to the exchangeable fraction fits with the TF of the most available metals. The poor agreement between the two methods of evaluating metal availability could be due to different plant species or other still unclarified factors. TF [plant/sediment] succession in decreasing order is: Cr – Hg – Ni – Mo – Co, Sb – As, Ni – Cd – Ag – Zn – Cu – Pb – Bi.

The TF REE [plant/sediment] was generally very low (Table 4) and ranged from 0.01 (Tm) to 0.34 (La, Ce), which reflects very low mobility capacity from the lake sediments to the studied plant species. Although the sequential extraction scheme indicates that all REEs are heavily bound to the exchangeable fraction, the percentage of each REE in this fraction is very low. Thus, REE in lake sediments does not pose any harm to the studied plant species.

T a b l e 4

Basic statistics TF [PTE, REE] in relation of plants to lake surficial sediments

Element (TF sediment)	Valid N	Mean	Minimum	Maximum	Std. dev.
Cr	12	4.62	1.23	20.83	5.51
Co	12	0.19	0.06	0.58	0.17
Mo	12	1.47	0.57	5.61	1.42
Cu	12	0.08	0.02	0.32	0.09
Pb	12	0.04	0	0.24	0.07
Zn	12	0.09	0.01	0.37	0.11
Ni	12	1.77	0.44	7.71	2.06
As	12	0.16	0.03	0.62	0.2
Cd	12	0.14	0	0.56	0.18
Sb	12	0.19	0.04	0.86	0.23
Bi	12	0.03	0	0.15	0.05
Ag	12	0.1	0	0.44	0.14
Hg	12	2.91	0.92	9.07	2.27
Se	12	0.16	0.05	0.33	0.09
La	12	0.11	0.04	0.34	0.09
Ce	12	0.11	0.03	0.34	0.09
Pr	12	0.1	0.03	0.3	0.08
Nd	12	0.08	0.02	0.23	0.06
Sm	12	0.08	0.02	0.23	0.06
Eu	12	0.1	0.03	0.29	0.07
Gd	12	0.05	0.02	0.14	0.03
Tb	12	0.09	0.03	0.26	0.06
Dy	12	0.05	0.02	0.16	0.04
Ho	12	0.05	0.02	0.14	0.04
Er	12	0.06	0.02	0.17	0.04
Tm	12	0.04	0.01	0.12	0.03
Yb	12	0.05	0.02	0.14	0.03
Lu	12	0.04	0.02	0.13	0.03

In Table 5 mean, minimum, maximum and standard deviation of the calculated TF [plant/water] are presented, showing inconstant TF PTE values ranging from 0.00 (Se) to 1652 (Cr). Extremely raised TF values were noticed for the Cr (97.2 –

1652), while the next highest PTEs were Ni (5.11 – 76.4) and Hg (4.25 – 45.3). All these three PTEs also tended to be the highest in the TF [plant/sediment] relation. Of the rest, all (Co, Mo, Cu, Pb, As, Cd, Bi and Ag) except for Zn, Sb and Se were higher than 1, and were in the range of 1.15 to 4.52. Great agreement can be noted between TF [plant/sediment] and TF [plant/water], meaning that PTEs in both the studied media (water and sediments) are present in the same or similar forms.

According to Table 5, the calculated TF values indicate that REEs in lake water are much more available to the studied plant species than PTEs. All the calculated TF REE [plant/water] mean values, except for Tm (0.69), are above 1, and range from 1.52 to 43.5. As no exact explanations for REE influences on plant growth have yet been established, no comparison can be made at this time. But as REEs in all the studied media show only minor enrichment, probably no major damage can be expected in the plant/water relation.

T a b l e 5

Basic statistics TF [PTE, REE] in relation of plants to lake water

Element (TF H_2O)	Valid *N*	Mean	Minimum	Maximum	Std. dev.
Cr	12	332.86	97.24	1652.17	430.98
Co	12	4.52	1.32	14.63	3.65
Mo	12	2.21	1.07	8.9	2.16
Cu	12	3.08	0.98	6.39	1.95
Pb	12	2.25	0.2	6.77	2.38
Zn	12	0.75	0.23	2.24	0.56
Ni	12	16.6	5.11	76.37	19.2
As	12	4.42	0.78	18.81	5.87
Cd	12	1.15	0.09	2.71	1.09
Sb	12	0.6	0.11	1.77	0.47
Bi	12	1.86	0.19	5.33	1.83
Ag	12	1.55	0.06	5.61	2.02
Hg	12	17.64	4.25	45.33	12.64
Se	12	0.00	0.00	0.00	0.00
La	12	11.75	4.11	28.07	7.32
Ce	12	12.74	4.58	31.73	8.38
Pr	12	11.17	3.64	26.99	7.49
Nd	12	8.59	3.07	19.62	5.19
Sm	12	19.9	6.84	47.42	12.74
Eu	12	3.37	1.13	7	1.81
Gd	12	29.8	9.93	59.25	14.82
Tb	12	1.52	0.53	3.25	0.88
Dy	12	26.12	8.99	56.55	14.15
Ho	12	1.66	0.57	3.58	0.92
Er	12	43.54	15.69	96.31	24.57
Tm	12	0.69	0.24	1.58	0.39
Yb	12	33.14	11.97	78.24	18.82
Lu	12	4.57	1.68	10.74	2.58

4. CONCLUDING REMARKS

The PTEs (Cr, Cu, Pb, Zn, Ni, As and Cd) in the studied plant species show great enhancement in all samples and also exceed the recommended and allowable limits. This also closely coincides with the sequential extraction results, which show that majority of PTEs are highly bioavailable in normal conditions. REE were also studied in plant samples and reflect a very similar range among all samples. Generally, all REEs were in the safe range, according to currently known regulations.

Relations among PTE in sediment, water and different plant species demonstrate that not all PTE found their way from the sediment to the plant system. Furthermore, it seems that, apart from Cr, Mo, Ni and Hg, others were poorly available to plants. But on the other hand, the majority of PTE are, according to the TF, highly correlated with those from lake water, meaning that PTE in lake water are present in forms that are easily available to the studied plant species. TFs of REEs in the discussed samples show interesting correlations. REEs from lake sediments have extremely low availability to plants, while REEs from lake water are much more available to the studied plant species, even more so than PTE from both media.

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Р е з и м е

ПОТЕНЦИЈАЛНО ТОКСИЧНИ ЕЛЕМЕНТИ И РЕТКИ ЗЕМЈИ ВО РАСТЕНИЈАТА ОД БРЕГОТ НА ЕЗЕРОТО КАЛИМАНЦИ (СИ РЕПУБЛИКА МАКЕДОНИЈА)

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Клучни зборови: езеро Калиманци; геохемија; растителни видови; фактор на пренос

Присуството на потенцијално токсични елемменти (PTE) и елементи на ретки земји (REE) честопати е зголемено во животната средина, особено во непосредна близина на активни или напуштени рудници. Бидејќи североисточните делови од Република Македонија се богати со метални рудни наоѓалишта, очекувано е зголемено загадување во околните екосистеми. Североисточниот дел од земјата исто така е многу важна земјоделска област каде што се одгледуваат повеќе видови растителни култури кои се наводнуваат од локалните езера и реки. Во овој труд се фокусиравме на различни растителни видови кои растат на брегот на езерото Калиманци. Сите видови растенија се анализирани за PTE и REE. Резултатите открија дека содржината на PTE (Cr, Cu, Pb, Zn, Ni, As и Cd) во проучуваните видови растенија е силно зголемена во сите примероци и исто така ги надминува препорачаните и дозволени граници. Меѓутоа, REE имаат многу сличен опсег во сите примероци. Генерално, вредностите на сите REE се во сигурни граници согласно со постојните регулативи.